Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Reversed Crystal Growth of ZnO Microdisks

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Experimental Details

ZnO microdisks were synthesized following the procedure below. A glass slide was cleaned by wiping twice with a chem-wipe which had been soaked in distilled water and then allowed to dry at room temperature. 15.5 mg sodium citrate was dissolved in a 500 mL aqueous solution containing 20.0 mM zinc nitrate and 14.0 mM hexamethylenetetramine. The clean glass slide was placed (at an angle of approximately 60°) into a vial containing 20 mL of this solution. The vial was sealed and incubated at 60 °C for 10 days. After this incubation period, the slide was removed from the vial and another damp chem-wipe was used to wipe clean its top surface. The ZnO microdisks were expected to grow only on the bottom surface of the glass slide. The slide was then further cleaned by being submerged in a beaker of distilled water for 10 min and then transferred to another beaker of distilled water for a further 10 min before being allowed to dry at room temperature. Early stage growth specimens were also synthesized following the same procedure but with different incubation times of 1-, 2-, 3- and 5-days respectively.

For the selective dissolution of the centre of the microdisks, a glass slide covered with the as-synthesized hexagonal microdisks was placed into a vial containing a 20 mL aqueous solution of 20 mM zinc nitrate and 119.7 mM ethylenediamine. The vial was then sealed and incubated at 60 °C for 4 h. After this incubation period, the slide was washed by being submerged in a beaker of distilled water for 10 min and then transferred to another beaker of distilled water for further washing for another 10 min.

Powder X-ray diffraction (XRD) was performed on the glass substrates covered with the microdisks using a PANalytical Empyrean diffractometer, with Cu Kα radiation (λ = 1.5418 Å). The diffracted X-rays were detected using a position sensitive detector with a scan range of 5 - 80°. Analysis of the powder XRD patterns was carried out using the Highscore Plus software. Scanning electron microscopic (SEM) images of the specimens were obtained using a Jeol-JSM-6700F field-emission gun microscope, operating at 1 to 5 kV with gentle mode. To overcome the beam charge problem, the specimen surface was coated with a thin gold film. Transmission electron microscopic (TEM) images, selected area electron diffraction (SAED) patterns and high resolution TEM (HRTEM) images were attained using a Jeol JEM-2011 electron microscope fitted with a LaB_6 filament operating at an accelerating voltage of 200 kV. The TEM and HRTEM images taken during this project were recorded using a Gatan 794 CCD camera.

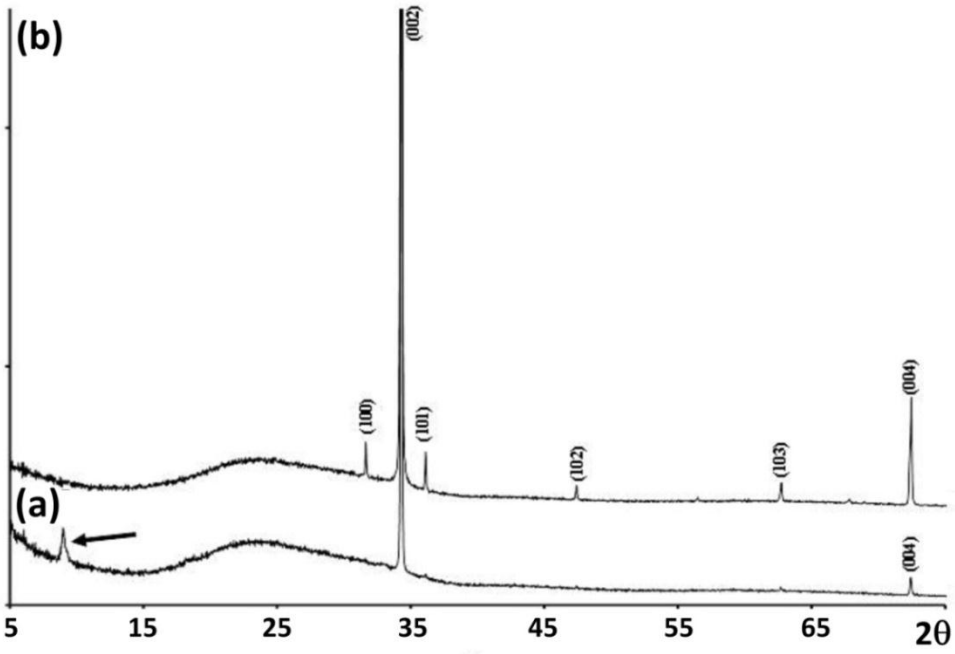

Figure S1. XRD patterns from microdisks grown with incubation periods of (a) 1 day, and (b) 3 days. Both patterns are indexed to hexagonal ZnO. The broad peak located at 2θ = 9.03° (marked by arrow) in pattern (a) can be indexed to the (200) plane of monoclinic $Zn_5(NO_3)_2(OH)_8.2H_2O$.

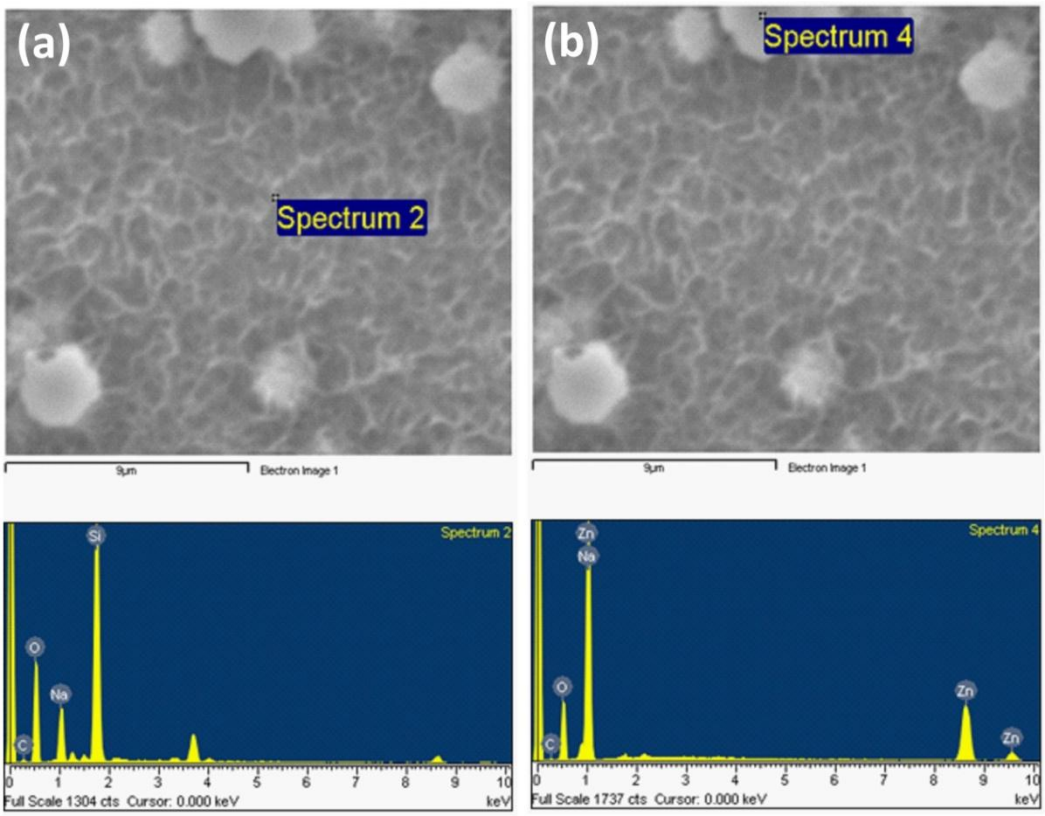

Figure S2. SEM images of clusters of ZnO precursor molecules on a glass substrate with corresponding EDX spectra shown below. The locations for the EDX collection are marked, (a) on the polymer film and (b) on a cluster. The Si peak in (a) is from the glass substrate.

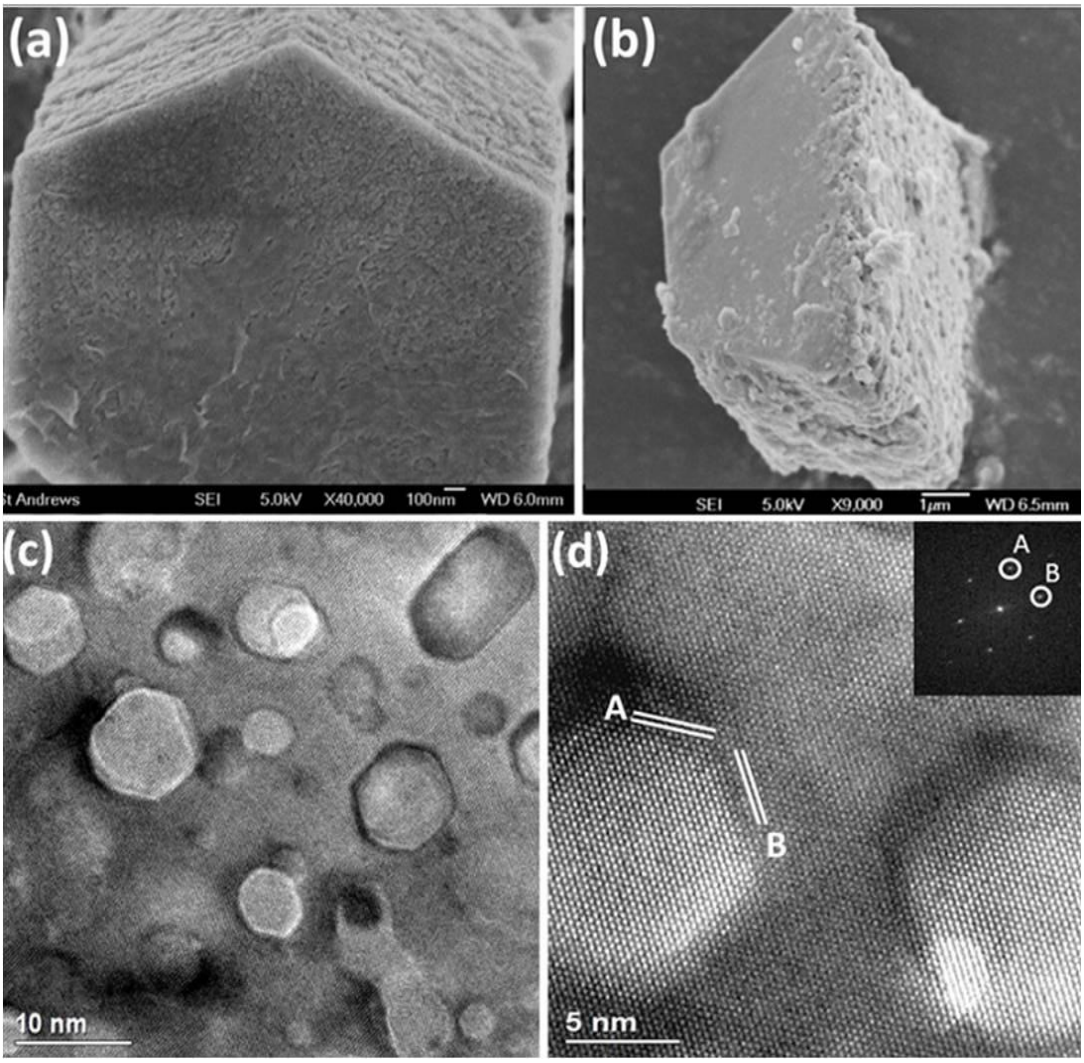

Figure S3. (a) SEM image of a hexagonal particle standing on the (0001) plane with partially crystallized surfaces, recorded from the 3 day sample. (b) SEM image of a half hexagonal particle with a rough surface on the right, implying the particle grew on the [$10\bar{1}0$] direction. (c) Low and (d) higher magnification HRTEM images and corresponding FFT pattern (inset in d) of the top surface plate of a hexagonal microdisk imaged from the 3 day sample, displaying many holes with a lighter mass-thickness contrast inside the crystal. The measured d-spacings marked as A and B are 2.76 Å and 2.77 Å with the interplane angle of 120º, which can be indexed to the ($01\bar{1}0$) and ($10\bar{1}0$) planes of the ZnO unit cell, indicating that the view direction is along the [0001] zone axis.

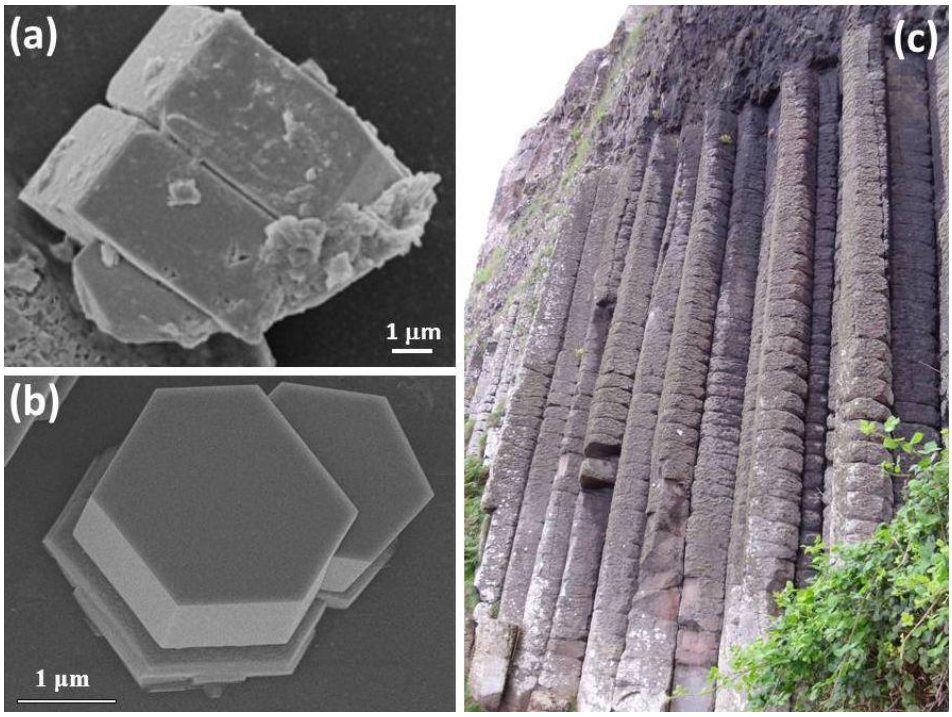

Figure S4. (a,b) SEM images of hexagonal ZnO microdisks showing the double-block structure. (c) Photo showing the massive stone pillars, made up of many hexagonal blocks, at the Giant's Causeway in Northern Ireland.

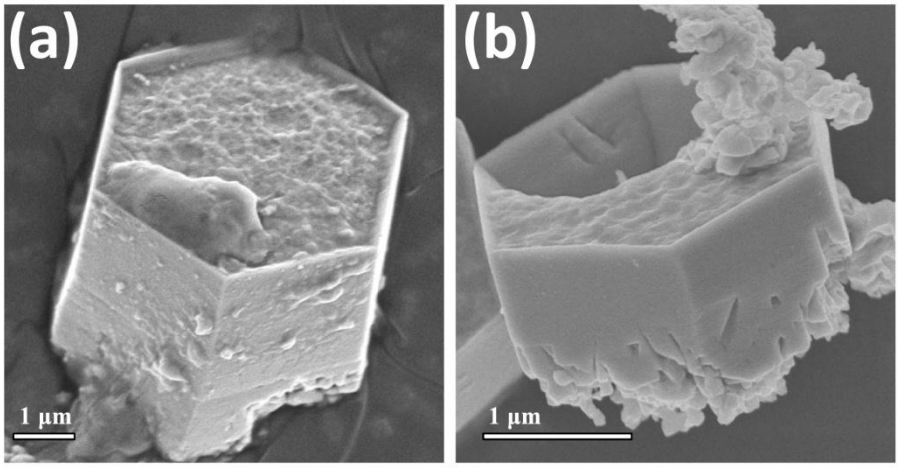

Figure S5. SEM images of ZnO microdisks recorded at different stages of selective dissolution to develop microstadium particles. (a) Initially the top (0001) ZnO shell is removed exposing the intact disordered core. (b) Partial removal of the polycrystalline core leaving the single crystalline walls undamaged.